

## Procedures to the production of Kompositmaterialien with high interface interest and thereby available Kompositmaterialien

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### Abstract of DE19540623

The invention concerns a method of producing composites with a high interface portion, in which a matrix of optionally surface-modified filler particles having affinity for the matrix phase and a particle size of more than 200 nm is incorporated in an amount of at least 5 vol %, such that the filler particles are distributed in the matrix phase in a substantially agglomerate-free state. Preferably at least 30 vol % of the matrix phase of the composites produced in this way is in the form of an envelope which surrounds the filler particles and differs from the remainder of the matrix phase in terms of its structure and properties. The high portion of interfacial phases in this composite imparts to this material properties which differ significantly from those of a corresponding composite which has only a slight, or no, interface portion.

### Description of DE19540623

In the early 80s years it was found out that nanokristalline crystals if they are kompaktiert about dispose relatively high interface volume which lends special qualities to the materials. Nevertheless, this was found only for materials which contain as the only phase a nanokristalline phase with which the nanokristallinen particles touch more or less. Beside metals initial investigations were also carried out in nanokristallinen ceramics with which, nevertheless, similar effects were not ascertained if one refrains of some temporary results which pointed to a raised Deformierbarkeit. Up to now similar phenomena were not ascertained in Kompositmaterialien with nanoskaligem construction, especially not with the compounds in which the matrix phase shows structures similar to polymer. Indeed, it is, e.g. famously, that in interfaces between polymers and metals by the effect of the interface divergences of the continuum structure of the polymers appear; nevertheless, the interface volumes with the usual materials are too low to change in any way the quality profile which consists more or less additiv of the single components. With the full polymers of usual kind with which interfaces appear between the filler particles and the polymers no appreciable influence of the interfaces on the material qualities could be ascertained up to now. By use of nanoskaliger fillers (e.g., disperse silicic acid) such effects were not likewise ascertained up to now, presumably because the used volume filling degrees were not sufficient to the production of interface influence or the interfaces showed no suitable structure or the conurbation degrees were too high. No suitable effects were found even with specific investigations to the production of Nanokompositen in the inorganic-organic systems with which

was postulated that special interfaces have appeared.

Astonishing proofs can be provided erfindungsgemäss materials which differ from the state of the technology by a very high interest in nanoskaligen particles and which have a clear influence of the interfaces on material and material qualities if necessary also by a certain interface arrangement. In such materials divergences are found by the qualities to be expected which can be led back only on interface phases. If one determines, e.g., the coefficient of expansion of certain such systems, one ascertains, this is clearly stronger reduced than this would be to be explained by the additiven effect of matrix and filler. Similarly it behaves with the elasticity module above  $T_g$  which is raised as a function of the filling degree clearly non-linear i.e. the E module lies at a substantially higher level than this is found with full polymers with similar volume filling degrees.

Similar consequences are also observed on the temperature position of the transformation area. If one fills, e.g., Aramidssysteme with  $ZrO_2$ , the transformation area from the area of 300 C DEG moves in the area of 400 C DEG, and at volume filling degrees in the area of 10% what is not to be explained with "filling" the polymer matrix with inorganic filler in the usual sense. Ähnliche results were found with  $SiO_2$ -full Methacrylatpolymeren or Methacrylat-Epoxy-Copolymeren.

With the help of the erfindungsgemässen procedure it is possible to produce Komposite whose behaviour not as usual additiv is determined by the qualities of both components (e.g., inorganic dispergierte phase on the one hand and organic or organically modified inorganic matrix, on the other hand), but by the interface phase. Without wanting to be bound to a certain theory, is supposed that the interface phase disposes of a structure with higher ordinal degree than the surrounding matrix. A direct structural analysis is not possible nowadays yet, because there are no methods with which these structures can be proved in the ready Komposit exactly.

The object of the present invention is demgemäss a procedure to the production of Kompositmaterialien with high interface interest with which one is marked a nanoskaligen filler in a polymeren matrix dispergiert and thereby that one to the matrix if necessary surfaces-modified filler particles with affinity do not so annex to the matrix phase and a particle size from more than 200 nm in an amount from at least 5 per cents by volume that the filler particles are distributed in state agglomeratfrei basically in the matrix phase.

By this procedure available Kompositmaterialien with high interface interest are likewise an object of the present invention.

The essential signs of the erfindungsgemässen procedure are therefore that in a certain minimum in the matrix phase nanoskaligen filler particles to be annexed an affinity show to the matrix phase and that they are distributed agglomeratfrei in the matrix phase. Only so can be made sure that in the Kompositmaterialien a high interface interest is, i.e. a high percentage of the matrix phase in the education of interface phases takes part which differ from the rest of the matrix phase (whose structure of that one unfull matrix resembles) in her structure and in her qualities. These interface phases surround the filler particles as it were like a cover. Their interest can be determined with organic polymers as a matrix, e.g., by the fact that one solves the matrix of the Kompositmaterials under surroundings terms with a solvent for the matrix phase so far as possible. The part of the matrix phase which cannot be solved any more shows the interface phase, i.e. the part of the matrix which has stepped with the filler particles in (strong) interaction. With this interaction it can be able to come to itself around kovalente connections between in the surfaces of the filler particles to located groups (which also from surfaces modification means used if necessary) and with it to reactive groups in the matrix molecules as well as around not kovalente interaction as for example dipole dipole interaction and electrostatic attraction acts. Therefore affinity to the matrix phase " the ability of the filler particles is to be known by the concept " how to enter the abovementioned or similar interaction with the molecules of the matrix phase which are strong enough to cause a certain orientation of the matrix molecules in the immediate neighborhood of the surfaces of the filler particles and to provide at the same time for

a connection or at least a strong attraction between the surface of the filler particles and the molecules of the matrix phase. This affinity between filler particle and matrix phase also provides for the fact that the filler particles are basically in isolation of each other, i.e. without education of Agglomeraten from several primary particles, in the matrix phase. This guarantees that the contact surface looks maximum between filler particle and matrix phase - and therefore also the interface phase - under the given conditions.

As already on top mentioned, was found erfindungsgemäss astonishing-wise that one can generate with agglomeratfreiem installation of nanoskaliger particles in organic or organically modified inorganic polymere matrixes a qualitative jump unknown till then in the e.g. mechanical and thermo-mechanical qualities which improves the use qualities of such Kompositmaterialien with lasting effect.

Decisively for the fact it is that one the nanoskaligen filler as an agglomerated powder do not separate in form of a stabilised, suspension agglomeratfreien (basically) in the matrix phase integrates and (if necessary by a suitable surface modification of the particles) maintains the agglomeratfreien state also in the final Kompositmaterial. This happens, e.g., by an adaptation of the polarity of matrix and filler particle. However, in this manner matrix and filler particle also step in relatively strong interaction relations which lead to interface structures in the ready Kompositmaterial which are presumably responsible for the observed qualitative quality changes. Helpfully the use of mechanical forces can also be as for example a mole effect with concurrent application of surfaces-modifying substances. The nanodisperse installation presumably affects in double way:

On the one hand, he leads to interaction between particles and matrix which change the matrix material in the internal interfaces to the particles and lead thus to the internal interface structure with new qualities. On the other hand it is caused by the nanoskaligen installation that the volume interest of these internal interfaces in the whole Kompositmaterial becomes so big by the big surface of the Nanopartikel that the quality changes (bereichen) to the interfaces to be ascribed become also clearly observeable makroskopisch.

One reaches this kind of the Nanokompositierung, e.g., by the fact that one goes out either from naturally agglomerated powders and breaks by Dispergierung in a suitable medium (foreign to matrix) the soft Agglomerate permanently (e.g., under use of Methacrylsäure (estern)), or that one uses from the start stabilised nanoskalige suspension (e.g., pebble sole). Nevertheless, also here is vital that one maintains the agglomeratfreien state in the ready Kompositmaterial (e.g., by suitable surface modification) to realise the causal chain described on top to the production of the new qualities.

Erfindungsgemässen Kompositmaterialien distinguish themselves especially by the fact that they expel new mechanical and thermo-mechanical qualities by an internal interface phase, e.g., a reduced thermal coefficient of expansion and a raised temperature permanence, and her optical qualities are adjustable by the Nanopartikel in wide areas; in particular it is possible to realise absolutely clear Kompositmaterialien in spite of high filling degree.

As erfindungsgemäss applicable materials for the matrix phase any known organic and inorganic polymere substances are suited. Also organically modified inorganic polycondensates are applicable as a matrix phase.

Examples for erfindungsgemäss especially advantageously applicable matrix materials are polyacrylic acid, Polymethacrylsäure, Polyacrylate, polyacrylamides, Polycarbamide, Polymethacrylate, Polyolefine, polystyrene, polyamides, Polyimide, polyvinyl connections like polyvinyl chloride, polyvinyl alcohol and Polyvinylbutyral, suitable Copolymere, e.g., Poly (ethylen-vinylacetat), polyester, e.g., Polyethylenterephthalat or Polydiallylphthalat, Polyacrylate, Polycarbonate, Polyether, e.g., Polyoxymethylen, Polyethylenoxid or Polyphenylenoxid, Polyetherketone, Polysulfone, Polyepoxide, fluorine polymers, Polysiloxane, Organopolysiloxane or with metals and transitional-metal educated Heteropolysiloxane as they are described, e.g., in

EP-A-36648 and EP-A-223067, as well as mixtures by two or several these polymers, as far as they are acceptable with each other. Instead of the called polymers can be also used their Oligomere and/or preliminary stages (monomers).

The nanoskaligen filler particles erfindungsgemäss to be used are mainly (at least partially) of inorganic nature.

With the nanoskaligen inorganic particles it concerns, e.g., oxide like CaO, ZnO, CdO, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, SnO<sub>2</sub>, PbO, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>; sulphides like CdS and ZnS; to selenide like gases, CdSe or ZnSe; Telluride like ZnTe or CdTe; Halogenide like NaCl, KCl, BaCl<sub>2</sub>, AgCl, AgBr, AgI, CuCl, CuBr, CdI<sub>2</sub> or PbI<sub>2</sub>; Carbide like CeC<sub>2</sub>; arsenide like AlAs, GaAs or CeAs; Antimonide like InSb; Nitride like BN, AlN, Si<sub>3</sub>N<sub>4</sub> or Ti<sub>3</sub>N<sub>4</sub>; Phosphide like GaP, InP, Zn<sub>3</sub>P<sub>2</sub> or Cd<sub>3</sub>P<sub>2</sub>; Carbonate like Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>; Carboxylate, e.g., acetates like CH<sub>3</sub>COONa and Pb (CH<sub>3</sub>COO) <sub>4</sub>; phosphates; sulphates; Silicate; Titanate; Zirkonate; Aluminate; Stannate; Plumbate and suitable mixing oxide, e.g., binary, tertiäre or quaternäre combinations of SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Likewise, e.g., mixing oxide with Perowskit structure is suited like BaTiO<sub>3</sub> or PbTiO<sub>3</sub>. In addition, modified inorganic particles as for example partikuläre Polymethylsiloxane, methacrylfunktionalisierte oxide particle and salts of the methyl phosphorus acid can be used organically. However, the metal colloids which can be usually produced about the reaction by metal salts and surface modification with ligands like Aminosilanen, Mercaptosilanen etc. (e.g. Au, Ag, Pt, Cu, Co, Ni, Pd) can be also used.

The production of this nanoskaligen particle can occur in usual way, e.g., through Flammhydrolyse, Flammpyrolyse and plasma procedure [see A.N.Dubrovina et al., Kristallografiya, 26 (1981) 637-639], colloid technologies [see E. Matijevic, "Preparation and Interaction of Colloids of Interest in Ceramics" in "Ultrastructure Processing of Advanced Ceramics", Hsg. : J.D.Mackenzie, D.R. Ulrich, John Wiley and Sons, New York (1988) 429, and other publications from E. Matijevic et al.] Sol gel processes [see R. Wet, H. Schmidt, journal of Non-Crystalline Solids 121 (1990) 329-333; M.A.Anderson et al., journal of membrane Science, 39 (1988) 243-258], controlled Nucleations-and growth processes [see e.g. L. Spanhe and M.A.Anderson, J. Admiral. Chem. Soc. 113 (1991) in 2826-2833; Iler, The Chemistry of Silica, Wiley and Sons, New York in 1979], MOCVD-procedure [see G.B.Springfellow "Organometallic Vapor Phase Epitaxy ; Theory and Practice", Academic Pressing, New York (1989), emulsion procedures [see DE 4118185 A1] and in the DE 41 30 550 OW and DE 41 33 621 A1 to described procedures.

The nanoskaligen particle have a particle size of maximum 200 nm, mainly from 2 to 50 nm and in particular from 5 to 20 nm. They exist mainly of inorganic materials with low thermal coefficient of expansion and materials with a coefficient of expansion  $<10 \cdot 10^{-6} \text{ K}^{-1}>$  are especially preferred. A very low thermal coefficient of expansion of  $5 \cdot 10^{-7} \text{ K}^{-1}$  have, e.g., SiO<sub>2</sub> particle which own the additional advantage of a thixotropen effect with the Dispergieren in the polymeren matrix. This thixotrope effect is presumably based on the education of a perkolierenden scaffolding with which the particle are with each other in touch. The viscosity-changing qualities of the nanoskaligen particles can be put by suitable surface modification. Especially BAVARIANS, SnO<sub>2</sub> sole of the fa are preferred stabilised colloid, nanodisperse sole of inorganic particles as for example pebble sole of the fa. Goldschmidt, TiO<sub>2</sub> sole of the fa MERCK, SiO<sub>2</sub>-, ZrO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>-, Sb<sub>2</sub>O<sub>3</sub>-sole of the fa Nissan Chemicals or Aerosildispersionen of the fa DEGUSSA.

The volume interest of the nanoskaligen particles in the Kompositmaterial normally amounts to from 5 to 50 Vol.-%, mainly from 10 to 30 Vol.-% and in particular from 15 to 20 Vol.-%, referring on filler plus matrix.

For the surface modification of the nanoskaligen particles, e.g., the materials which can fulfil several functions (partly in parallel) can be used. They are able to, e.g.

1. Prevent the conurbation of the particles with the Kompositherstellung;
2. The rheologische behaviour of the Komposite also at very high filling degrees (e.g., 20 Vol. - %) adapt by adjusting of the change efficacies between the particles and the matrix and/or other neighbouring particles to the requirements;
3. In spite of very high filling degrees maintain the transparence of the filler, above all, in the VIS NIR area;
4. By reactions with the matrix and/or other particles mechanical, thermo-mechanical and adhäsiven or kohäsiven qualities of the Kompositmaterialien in the ready (hardened) state in wide areas put.

As a surface modifier will react mainly surfaces-modifying low-molecular organic (= carboniferous) the connection which disposes of at least one functional group which is able to with in the surface of the filler particles to available groups and the polymeren matrix and/or (at least) wechselwirken used. For this purpose are suited in particular connections with a molecular weight which is not higher than 500, mainly not higher than 350 and in particular not higher than 200. Such connections are liquid mainly under normal terms and show mainly no more than a total of 15, in particular no more than a total of 10 and especially prefers no more than 8 carbon atoms. The functional groups which must carry these connections are directed, primarily, after the surface groups of the nanoskaligen particle used in each case and, in addition, also after the desired interaction with the matrix. Thus an acid / base reaction can take place, e.g., between the functional groups of the surfaces-modifying connection and the surface groups of the filler particles to Bronsted or Lewis (including complex education and Adduktbildung). An example of another suitable interaction is the dipole dipole interaction. Examples of suitable functional groups are carboxylic acid groups, (primary, secondary, tertiäre and quartäre) amino groups and C-H-acide groupings. Several these groups can also exist at the same time in a molecule (Betaine, amino acids, EDTA, etc.).

Demgemäss are examples of preferential surface modifiers saturated or unsaturated mono carboxylic acids and polycarboxylic acids (mainly mono carboxylic acids) with from 1 to 12 carbon atoms (e.g., formic acid, acetic acid, Propionsäure, butyric acid, pentane acid, Hexansäure, acrylic acid, Methacrylsäure, Crotonsäure, citric acid, adipic acid, succinic acid, Glutarsäure, oxalic acid, Maleinsäure and Fumarsäure) as well as their Ester (mainly C1-C4-Alkylester) and Amide, e.g., Methylmethacrylat.

Examples of other suitable surface modifiers are quartäre ammonium salts of the formula  $\text{NO. } <1 \text{ R } <2> \text{ R } <3> \text{ R } <4> + \text{X}$  in what  $\text{R } <1>$  to  $\text{R } <4>$  explain if necessary of each other different aliphatische, aromatic or cycloaliphatische groups with mainly from 1 to 12, in particular to from 1 to 6 carbon atoms and X  $\leftrightarrow$  stands for an inorganic or organic anion; mono amine and polyamine, in particular such of the general formula  $\text{R}_3\text{-nNHn}$  in what  $n = 0, 1 \text{ or } 2$  and the rests R independently of each other Alkylgruppen with from 1 to 12, in particular from 1 to 6 and especially prefers to from 1 to 4 carbon atoms shows (e.g., methyl, Ethyl, n- and i-Propyl and Butyl) and Ethylenpolyamine (e.g., Ethylendiamin, Diethylentriamin etc.); Amino acids; Imine; beta-Dicarbonxylverbindungen with from 4 to 12, in particular to from 5 to 8 carbon atoms, as for example Acetylaceton, 2,4-Hexandion, 3,5-Heptandion, Acetessigsäure and Acetessigsäure-C1-C4-alkylester; Silane, in particular Organoalkoxysilane, as for example those which are used for the surface modification by colloid silicic acid (e.g., such of the general formula  $\text{R}_4\text{-mSi}$  (OR min) m in what the groups R and R min independently of each other C1-C4-Alkyl explain and m 1, 2, 3 or 4 is); and modified Alkoholate with which a part of the OR groups (R as on top defined) is substituted for inert organic groups.

To the electrostatic stabilisation of the nanoskaligen filler particles can be used, e.g., also the connections known for this purpose as for example NaOH,  $\text{NH}_3$ , KOH,  $\text{Al}(\text{OH})_3$ , provided that they are acceptable with the polymeren matrix.

The ready polymers (and/or their basic materials) for the matrix, the nanoskaligen filler particles

and (if necessary) the surfaces-modifying materials can be used either as those or mainly as a solution in an organic solvent and/or in water. Examples of suitable solvents are alcohols like Butanol, Ketone like acetone, Ester like ethyl acetate, Ether like Tetrahydrofuran and aliphatische, aromatic and halogenierte hydrocarbons like Hexan, benzene, toluol and chloroform.

The production erfindungsgemässen Kompositmaterialien can occur in different way.

For example, one is able to do the nanoskaligen particle in one of the abovementioned solvents and/or one abovementioned polymerisierbaren or härtbaren connections dispergieren, e.g., under touching or by means of ultrasound. Then the preserved dispersion becomes with the polymer (or his basic materials) for the matrix either as such or dilutes with a solvent mixed. The solvent used for diluting is mixable either identically with the solvent used for the dispersion or with it. Of course can become the nanoskaligen particle also in a solution of the polymer or his basic materials dispergiert. Alternatively the polymer or the connections delivering the polymer can be solved in a stabilised dispersion (watery or non-watery) of the nanoskaligen particles or be mixed, if necessary under addition of the surfaces-modifying materials.

In case of the use from (organic) polymerisierbaren or härtbaren connections the Kompositmaterial contains further a Polymerisations-catalyst, polyaddition catalyst and/or polycondensation catalyst which can induce the interlinking and Härtung thermally and/or photo-chemically (collectively as an "interlinking initiator" called).

As photo initiators, e.g., the starters available in trade can be used. Examples for this are Irgacure a TM 184 (1-Hydroxycyclohexylphenylketon), Irgacure TM 500 (1-Hydroxycyclohexylphenylketon, Benzophenon) and other from the company Ciba g of available photo initiators of the Irgacure Tm type; Darocur TM 1173, 1116, 1398, 1174 and 1020 (available from the company Merck), Benzophenon, 2-Chlorthioxanthon, 2Methyl-thioxanthon, 2-Isopropylthioxanthon, Benzoin, 4.4 min-Dimethoxybenzoin, Benzoinethylether, Benzoinisopropylether, Benzoyldimethylketal, 1,1.1-Trichloracetophenon, Diethoxyacetophenon and Dibenzosuberon.

When thermal initiators come and a. organic Peroxide in the form of Diacylperoxiden, Peroxydicarbonaten, to Alkylperestern, Dialkylperoxiden, Perketalen, Ketonperoxiden and Alkylhydroperoxiden to question. Concrete examples of such thermal initiators are Dibenzoylperoxid, tert.-Butylperbenzoat and Azobisisobutyronitril.

The interlinking initiator is covered, if used, normally in an amount from 0.1 to 5, mainly from 0.5 to 3 weight percent, to the called composition, is applied.

For the rise of the viscosity or to the production of Komposite free of solvent the solvents can be removed partially or completely.

Then the ready Kompositmaterial can be processed in usual way, e.g., by education of a form body or applying on a substrate in form of a coating, if necessary followed from a drying and/or Härtung.

If the Kompositmaterial contains a linkable up connection, this is linked up as a function of the kind of the used interlinking initiator thermally and/or by radiotherapy (e.g., with an UV lamp or a laser) and is hardened.

The Härtungsbedingungen (temperature, UV wavelength etc.) are directed after the decay terms of the interlinking initiator.

In the Kompositmaterial available by the erfindungsgemässe procedure mainly at least 30 per cents by volume of the matrix phase are in form of an interface phase, i.e. of a cover surrounding the filler particles which differs from the rest of the matrix phase concerning her structure and her qualities. Especially preferentially the interface phase puts out at least 50 and in particular at least

75 per cents by volume of the whole matrix phase. An interest of the interface phase is still more preferential in the matrix phase of at least 90 and in particular at least 95 per cents by volume.

The following examples should explain the present invention further without limiting them, nevertheless, in any way.

#### Example 1

8.05 ml colloid, watery Kieselsol (NISSAN-Snowtex, 50 weight percent SiO<sub>2</sub>, particle size approx. 20 nm) are strongly stirred with 10.5 ml Tetraethoxysilan (TEOS) and afterwards 0.212 are added ml concentrated hydrochloric acid. In an exothermen reaction the 2-phase mixture becomes by educated Ethanol at from approx. 2 to 4 minutes einphasig. About 2 minutes after occurred Homogenisierung 15, 26 ml gamma-Glycidoxypopyltrimethoxysilan (GPTS) are added and it is stirred 2 other hours. As a result are added for the purpose of thinner 30 ml Ethanol. Before the use of the resultant mixture as a coating composition 0.56 are added ml Methylimidazol as a starter of the Epoxy interlinking. With the resultant composition become Polycarbonat records (10x10 cm; Bayer-Apec HT) by Rakeln coats (layer thickness from 20 to 50  $\mu$ m) and the resultant coating is condensed with 160 C DEG during 6 hours thermally.

The coating shows before black background with Auflicht a light Trübung. The scattered light increase after 1000 cycles Taber Abraser test (CS 10fa, 500 g) amounts to from approx. 3 to 4%.

#### Example 2

The procedure of example 1 is repeated, however, are used instead of Methylimidazol 5 ml of a mixture of 94.2 ml gamma-Aminopropyltriethoxysilan (APTES) and 60.27 ml to alcoholic SiO<sub>2</sub>-Sol (NISSAN, MA Saint, 30 weight percent SiO<sub>2</sub>, particle size about 10 nm) as a starter of the Epoxy interlinking (component system two).

The resultant coatings show before black background with Auflicht a light Trübung. The scattered light increase after 1000 cycles Taber Abraser test (CS 10fa, 500 g) amounts to from approx. 4 to 5%.

#### Example 3

20 ml APTES and 20 ml alcoholic SiO<sub>2</sub>-Sol (see example 2) are mixed and stirred during 2 hours. Afterwards 7.43 gs Pyromellitsäuredianhydrid and 1.4 ml water are added. The mass tough in the beginning liquefies within less minutes and can be used for coating. The coating and compression occur like in example 1.

The resultant coatings are clear, yellowish and show a Photochromie from yellowish after green in the sun and ultraviolet light.

The Streulichzunahme after 1000 cycles Taber Abraser test (CS 10fa, 500 g) amounts to from approx. 4 to 5%.

#### Example 4

a) Production of nanoskaligen TiO<sub>2</sub> particles (in alcoholic solvents)

57,10 gs n-BuOH are moved in 250 ml round piston with 51.73 gs Tetraethyltitanat. For the purpose of Hydrolyse and condensation of the titan alc. oxide one adds to the mixture slowly 5.55 gs HCl (37 weight percent) and touches afterwards 5 minutes with ambient temperature. Afterwards one moves the reaction mixture drop by drop with 3.76 gs of concentrated Perchlorsäure (60 weight percent) and stirs afterwards other 10 minutes. Niedrigviskosen, clear mixture one lets drip 9.82 gs Aluminiumtributanolat to.

b) Production of a watery Böhmit suspension

In 100 ml round piston one presents 66.42 gs 0.1 m HCl and then adds in helpings 6.64 gs Böhmit (Disperal Sol P3, fa Condea). Afterwards the suspension is treated during approx. 20 minutes with ultrasound.

c) Production of a Beschichtungssols

In 250 ml round pistons are mixed 16.96 gs Phenyltriethoxysilan, 83.46 gs GPTS and 29.47 gs TEOS and then are moved with 16.53 gs of watery Böhmit suspension (see (b) on top). The preserved reaction mixture is stirred 2 hours with ambient temperature on which to her under ice cooling this becomes made alcoholic TiO<sub>2</sub>-Sol zugetropft like on top under (a). The resultant mixture is stirred another 2 hours under ice cooling and then is moved with 56.53 gs of Böhmit suspension.

The clear Beschichtungssol is raised about standard coating procedure as for example catapult, diving coating and spray coating on plastic substrates. The age-hardening of the coating material occurs thermally with from 90 to 150 C DEG.

The scattered light increase after 1000 cycles Taber Abraser test (CS 10fa, 500 gs of edition) amounts less than 2%.

Example 5

gamma-Methacryloxypropyltrimethoxysilan (MPTS) is moved with 30 weight percent Böhmit and afterwards stöchiometrisch with 0.1 n HCl vorhydrolysiert. After approx. 20-hour stirring with ambient temperature the suspension milky in the beginning becomes clear and it originates transluzentes Sol. Afterwards the Sol with 2-Isopropoxyethanol comparatively becomes 1:1, covered to the eingewogene amount in MPTS, dilutes, in which itself the addition of Triethylenglykoldimethacrylat (TEGDMA) in the weight relation 1: 2 covered ough MPTS connects. In the end, 2 weight percent tert.-Butylperbenzoat were covered to MPTS + TEGDMA, were added. With the resultant coating composition Polycarbonat records are coated by diving coating in a layer thickness of from 8 to 9 µm. The coated substrates are hardened 3 or 20 hours with 150 C DEG in the dry cupboard. The scattered light increase after 1000 cycles Taber Abraser test (CS 10fa, 500 g) amounts approx. 4%. The scratch hardness is about 12 gs.

Example 6



The procedure of example 5 is repeated, with the exception that MPTS is substituted with GPTS and no TEGDMA is used (layer thickness from 5 to 6  $\mu\text{m}$ ).

The scattered light loss amounts to about 2% and the scratch hardness amounts to about 30 gs.

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#### Claims of DE19540623

1. Procedures to the production of Kompositmaterialien with high interface interest, with which one a nanoskaligen filler in a polymeren matrix dispergiert, thereby marked that one to the matrix if necessary surfaces-modified filler particles with affinity do not so annex to the matrix phase and a particle size from more than 200 nm in an amount from at least 5 per cents by volume that the filler particles are distributed in state agglomeratfrei in basically in the matrix phase.
2. Procedures after claim 1, thereby marked that the filler particles do not show a particle size from more than 50 nm and in particular no more than 20 nm.
3. Procedures after any of the claims 1 and 2, thereby marked that the filler particles of the matrix are annexed to an amount from at least 10 and in particular at least 15 per cents by volume.
4. Procedures after any of the claims from 1 to 3, thereby marked that the matrix is an organic one or an organically modified inorganic polymer or polycondensate.
5. Procedures after any of the claims from 1 to 4, thereby marked that the filler particles of inorganic nature are and are based in particular on oxide of Si, Ti, Zr, Al, Sn and/or Sb.
6. Procedures after any of the claims from 1 to 5, thereby marked that one produces the matrix in presence of the filler particles.
7. Procedures after any of the claims from 1 to 5, thereby marked that one removes the filler particles in one the matrix and if necessary surfaces modification means for the filler particles containing solution dispergiert and the solvent.
8. Kompositmaterial, available after the procedure according to any of the claims from 1 to 7.
9. Kompositmaterial after claim 8, thereby marked that at least 30 per cents by volume of the matrix phase are in form of a cover surrounding the filler particles which differs from the rest of the matrix phase concerning her structure and her qualities.
10. Kompositmaterial after claim 9, thereby marked that at least 50 and in particular at least 75 per cents by volume of the matrix phase are in form of the cover surrounding the filler particles.
11. use of the Kompositmaterials after any of the claims from 8 to 10 to the production of form bodies or coatings.